THE VARIATION OF COAL PYROLYSIS BEHAVIOR WITH RANK

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Coal pyrolysis is important since it is the initial step in most coal conversion processes and is the step which is most dependent on the properties of the coal. Recent reviews of the pyrolysis literature (1-3) present a complicated profusion of results in which it is difficult to identify any simplifying order. The purpose of this paper is to provide some understanding of the diversity in the reported data.

The problem of interpreting kinetic rate constants in coal pyrolysis is illustrated in Fig. 1 adapted from (2). The figure presents a summary of reported rate constants (4-21) for weight loss, most of which are derived assuming a simple first order process. Figure 1 shows that at any given temperature, there is between a two and four order of magnitude variation in reported rate constant, as well as wide variations in slope (acitvation energy). For coal pyrolysis in the absence of external reacting gases, the possible causes for such variations are: 1) coal type; 2) the assumptions used for deriving a kinetic expression; 3) reaction conditions (reaction time, pressure, particle size, heating rate, final temperature and mass transfer rates).

A recent review, (22) considered whether coal type was a cause for such variation. A number of experiments were examined in which coal rank alone was varied. The conclusion of this review was that at low temperature, where chemical kinetic rates can be most easily measured, the rates for hydrocarbon evolution vary by at most a factor of 5 between lignite and bituminous coals. Significant rank variations were also absent in high temperature experiments. Therefore, rank variation is probably the least important cause for scatter.

One cause for variations in reported activation energy is the assumption of a single first order process when a number of parallel reactions with different rates contribute to weight loss. In this case, the use of a single rate constant will lead to anomalously low activation energies. If there are no heat transfer limitations, the rate constant will be reasonable at the temperature of the reaction. This problem has been discussed by a number of investigators (5,18,21-24).

The major causes for rate variations, therefore, appear to be heat and mass transfer limitations. To separate these effects from the chemical kinetic rate, coal pyrolysis was measured in two experiments designed to minimize heat and mass transfer limitations. Coals of different rank were used to provide additional data on rank variations. The first experiment is a constant heating rate experiment in which the coal is heated slowly enough (30°C/min) that heat transfer to the coal particle is not a problem. The major weight loss occurs at about 500°C. The second experiment provides for rapid heating (3 to 5 x 10^4°C/sec) so that weight loss occurs between 700 and 900°C.

The results of both experiments confirm that variations in coal rank cause at most a factor of 5 variation in the rate constant for weight loss. The latter experiment yields very high rates in line with those reported by Badzioch and Hawksley (4) and Freihaut (15). The result suggests that lower rates reported at these temperatures and comparable rates reported at higher temperatures were due to heat transfer limitations. That is, these experiments have measured the rate of heat transfer to the coal particle, not a chemical kinetic rate constant for weight loss.

SLOW HEATING EXPERIMENT

Pyrolysis was carried out by heating the coal in a wire grid rapidly to 150°C and then at approximately 30°C/min to 900°C. The grid is located within an infrared cell swept by 0.7 liter/min of nitrogen at 1 atmosphere. Infrared spectra of the

evolving products are obtained every 15 seconds with a Nicolet 7199 FT-IR. The spectra for pyrolysis of a coal maceral are illustrated in Fig. 2. Specific regions of the spectra are integrated to give the amounts of a particular gas in the cell as a function of time. The ordinate is proportional to evolution rate. The tar amounts are indicated by scattering of the IR beam which shifts the base line absorbance at high wavenumbers. While the tar measurement is not quantitative, it does indicate the onset, peak and conclusion of tar evolution.

Data for 10 coal samples are presented in Figs. 3 and 4. The data include one repeated experiment for a Pittsburgh Seam bituminous coal and samples of this coal which oxidized during 13 and 504 hours of drying at 110°C. The points are data from individual FT-IR spectra.

Tar evolution (Fig. 3) exhibits the narrowest peak. The rank variations in the temperature of the peak evolution are small. The lignites peak at about 490°C while the highest rank bituminous coals peak at about 530°C. This corresponds to about a factor of 5 in rate. The data can be modeled with a single source with a Gaussian distribution of activation energies (Fig. 3c). This approach to modeling individual species has been discussed previously (22-25). It avoids the anomanously low activation energies obtained from assuming a single first order process. The rate parameters for tar evolution are presented in Fig. 1. The second term in the exponent is the width of the gaussian. The tar rate plotted in Fig. 1 fits the bituminous and subbituminous coals best. It is a little low for the lignite.

The evolution data for heavy aliphatic gases are presented in Fig. 4. The peaks are slightly wider than for tar. The high temperature tail on the peak may be an artifact of the experiment which is caused by gas not immediately swept from the cell. This tail has not been modeled. Rank variations in the data are small. The lowest peak at 500°C is for a lignite and the highest at 540°C is for a high rank bituminous. Rank variations, therefore, can produce a factor of 5 variations in kinetic rate for heavy aliphatics. Aliphatic evolution is modeled in Fig. 4c. The rate parameters are presented in Fig. 1.

Tar and heavy aliphatics typically account for 50 to 75% of the volatiles and up to 90% of the initially released volatiles. Thus, on the basis of the above results, rank variation in initial volatile release must be small.

Data for additional species and analyses of the coals will be presented in (22). Similar rank insensitivity was observed for CH_4, CO, CO_2, C_2H_4 and H_2O.

RAPID HEATING EXPERIMENT

The reactor consists of a 1/4" diameter stainless steel tube which is heated electrically. Coal entrained in cold carrier gas is injected at the top of the tube. The coal is fed using a previously described entrainment system (23,25). The coal-gas mixture enters the heated section of tube and heats rapidly. The heat transfer rate is large because of the small tube diameter and the high thermal conductivity and small heat capacity of the helium carrier gas. After a variable residence time, the reacting stream is quenched in a water cooled section of tube. The product collection train was described previously (23,25). It consists of a cyclone to separate the char followed by a collection bag to collect the gas, tar and soot. The gas from the bag is analyzed by FT-IR and the solids and liquids are collected on the bag surface and in a filter.

The temperature of the gas has been measured with a thermocouple under conditions of constant tube current. At constant current, the tube will reach an equilibrium temperature such that the power radiated is equal to the electrical power input. With gas or coal flowing in the tube, the tube is initially cooler than the equilibrium temperature as heat is used to raise the temperature of the reactants. When the reactants reach the equilibrium temperature, the outside of the tube reaches a constant temperature, so the heating region is directly observable.

Figure 5a shows the measured gas temperature with no coal flow at a tube equilibrium temperature of 800°C. The gas velocity, coal velocity and coal particle temperature have been calculated (Figs. 5a, b and c) as functions of time and distance assuming that the coal provides no additional heat load, (in agreement with only a small change in the observed temperature of the tube exterior when coal is

introduced). The gas velocity is calculated from the measured temperature using the ideal gas law. The coal velocity is obtained by integrating the acceleration determined by applying Stokes and Newton's laws. The heat up time at 800°C is calculated to be approximately 18 msec. The heat up time at 900°C and 700°C are 16 msec and 21 msec respectively. The times required to get from 600°C to equilibrium temperature, are on the order of 3-5 milliseconds.

Results for a North Dakota lignite and an Illinois #6 coal are compared in Fig. 6. The data are for weight loss and aliphatic gas evolution. The aliphatic gas evolution data have been fit using the same rate (see Fig. 1) as for the low temperature experiment. The parameters which describe the species amount are the same as previously used to model these coals in the constant heating rate experiment (22) and in the entrained flow reactor (23,25). No attempt has been made to optimize the parameters for the new data. The fit is good for the Illinois #6 but could be improved with a higher rate (about a factor of 5) for the North Dakota lignite.

The weight loss data have been modeled (lines in Fig. 6c and d) using a previously described theory (23-25) which combines the weight loss due to the evolution of individual species (tar, paraffin, water, CO, etc). There is reasonable agreement with the data. To compare these data to the other data in Fig. 1, a single first order rate constant has been computed. The weight loss is dominated by the tar and aliphatic loss so this "rate constant for weight loss" should be between the rate for these two products as shown in Fig. 1. A minimum possible weight loss rate constant was derived by fitting the data as a single first order process assuming that the particles never accelerated above the initial cold gas velocity and were at the tube equilbrium temperature for the whole distance. This estimated rate is plotted on the low end of the vertical lines at 700, 800 and 900°C. The worst case assumptions, agree with Badzioch and Hawksley (4) and Freihaut (15) which were also done under conditions which favor high heat transfer. A higher rate is obtained by assuming that the coal is at the equilbrium tube temperature only for the time it takes to transit the hot section at the calculated velocity of the coal. This assumption over-estimates the rate because weight loss during heat up is neglected. This rate is plotted as the top of the vertical lines (700, 800, and 900°C). They fall between the aliphatic rate and the tar rate as expected.

DISCUSSION

Based on the information available it is possible to identify the probable cause for much of the scatter in Fig. 1. The data presented here confirm previous suggestions that coal kinetics are relatively insensitive to coal rank, ruling out rank variations as the cause. On the other hand, heat transfer limitations appear to be a primary factor. If the rate for tar evolution presented in Fig. 1 is correct, weight loss will be almost completed in 1 millisecond at 800°C. Any experiment which attempts to get data at higher temperatures must heat the coal from 600°C to the reaction temperature in less than 1 msec, requiring heating rates in excess of $2\text{-}5 \times 10^5$°C/sec. The weight loss measured in the entrained flow reactors at temperatures above 800° to 900°C (12,23,25) most likely occurs during particle heat up. Support for this suggestion comes from the observation that the better the heat transfer in the experiment, the higher has been the reported rate. The high heating rate experiments reported here have yielded the highest kinetic rates reported at 900°C. The new data are in reasonable agreement with the data of Badzioch and Hawksley (4) who used very fine coal and Freihaut (15) who dropped small amounts of coal alone, without cold carrier gas into a hot furnace. Both of these experiments provide high heating rates to moderate temperatures. Entrained flow reactor data of Maloney (19) and Solomon and Hamblen (26) show higher rates when helium (which has a high thermal conductivity) is used as the carrier gas rather than nitrogen. If weight loss occurs at temperatures less than the reactor temperature, the reported data would shift to lower temperatures.

This explanation runs into trouble for three experiments (14,16,20) which have measured the coal particle temperature during pyrolysis by two or three color

pyrometry. So, additional discrepancies exist which may be caused by such factors as mass transfer limitations or non-isothermal particle temperatures (a hot particle surface or hot soot or tar surrounding the particle). These possibilities must be examined in more detail.

CONCLUSIONS

1. Kinetic rates for individual species evolution in coal pyrolysis at low and high temperatures are relatively insensitive to coal rank.

2. High kinetic rates were measured at 700 to 900°C when the heat transfer rate is maximized.

3. Lower rates at these temperatures and comparable rates at higher temperatures which have been reported from heated grid and entrained flow reactor experiments were most likely heat transfer limited.

4. Comparable rates reported at higher temperatures in experiments which employ surface temperature measurements by two or three color pyrometry have not been explained.

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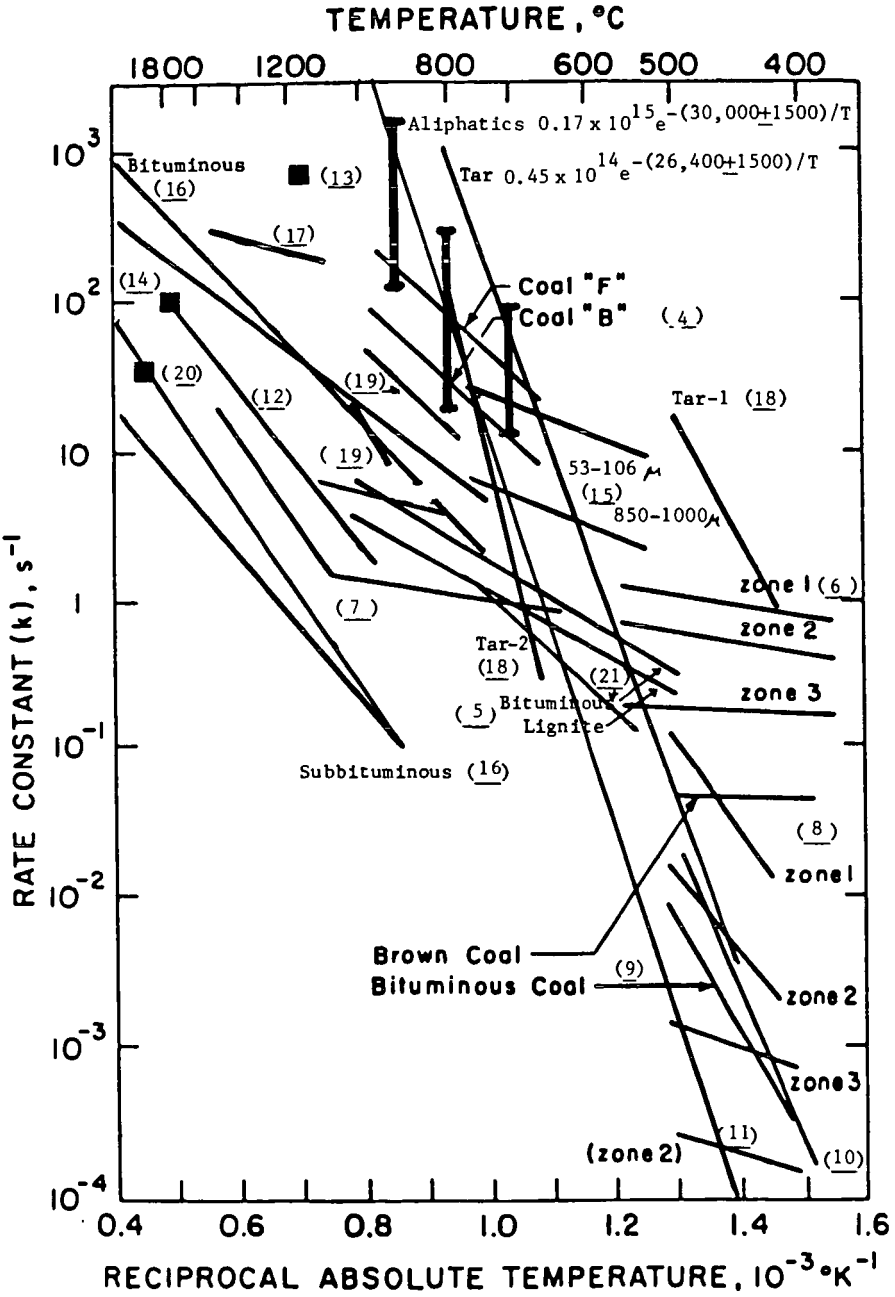

Figure 1. Comparison of Kinetic Rates for Weight Loss (or Tar Loss) from a number of Investigators.

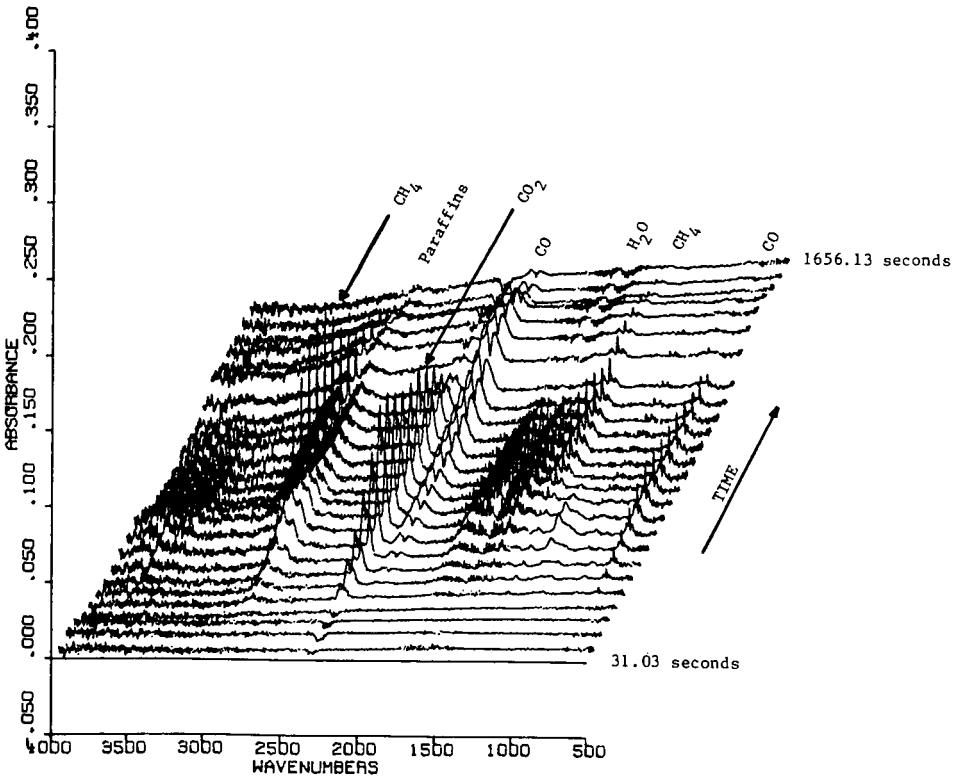

Figure 2. FT-IR Spectra obtained during Pyrolysis for a Pure Vitrinite Maceral in 1 Atmosphere of Nitrogen, Flowing at 0.7 liter/min. The Coal is Heated Rapidly at 150°C and at 30°C/min to 900°C.

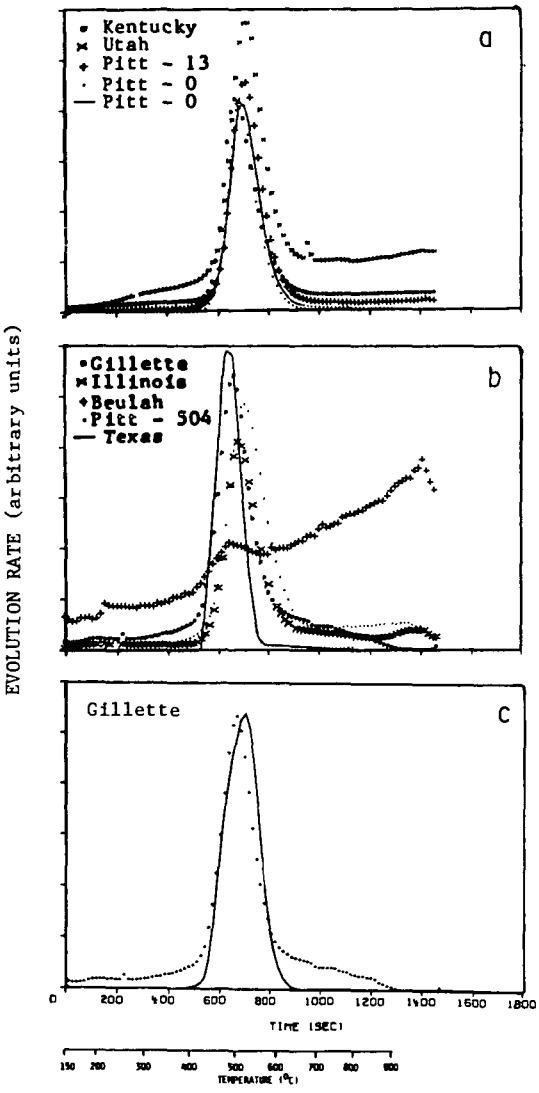

Figure 3. Evolution of Tar for 10 Coal Samples Pyrolyzed in 1 Atmosphere of Nitrogen, Flow ing at 0.7 liter/min. The Coal is Heated Rapidly at 150°C and at 30°C/min to 900°C.

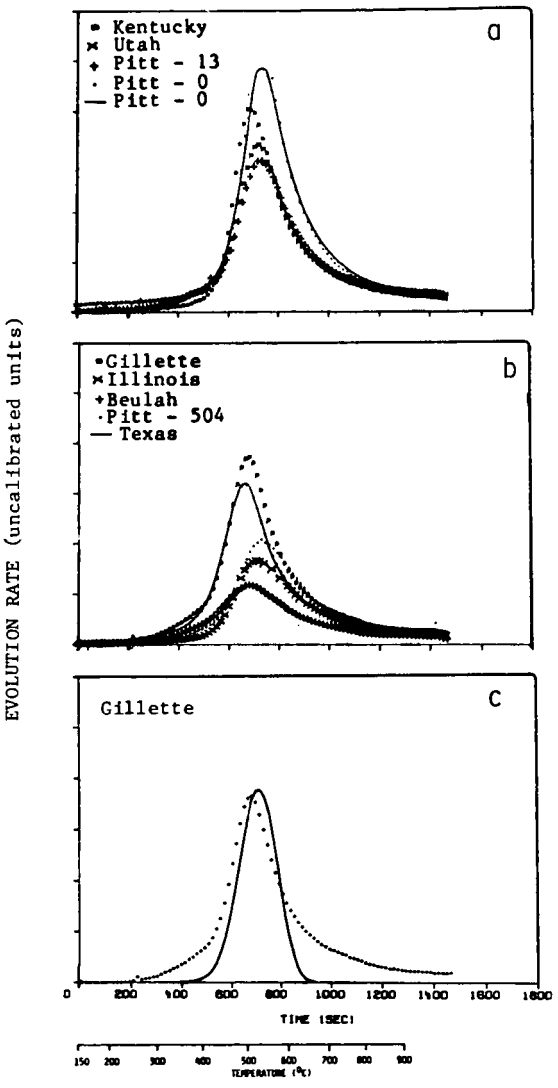

Figure 4. Evolution of Aliphatic Gases for 10 Coal Samples Pyrolyzed in 1 Atmosphere of Nitrogen, Flowing at 0.7 liter/min. The Coal is Heated Rapidly at 150°C and at 30°C/min to 900°C.

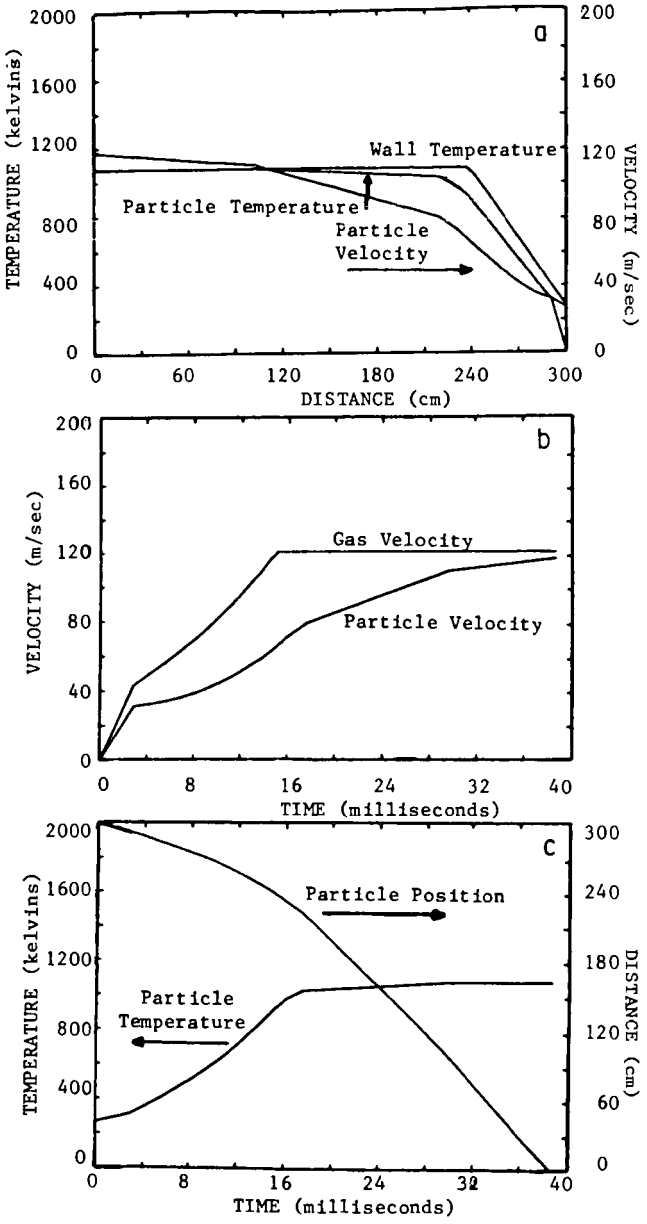

Figure 5. Measured Reactor Wall Temperature and Calculated Gas Velocity, Particle Velocity and Particle Temperature as Functions of Time and Distance.

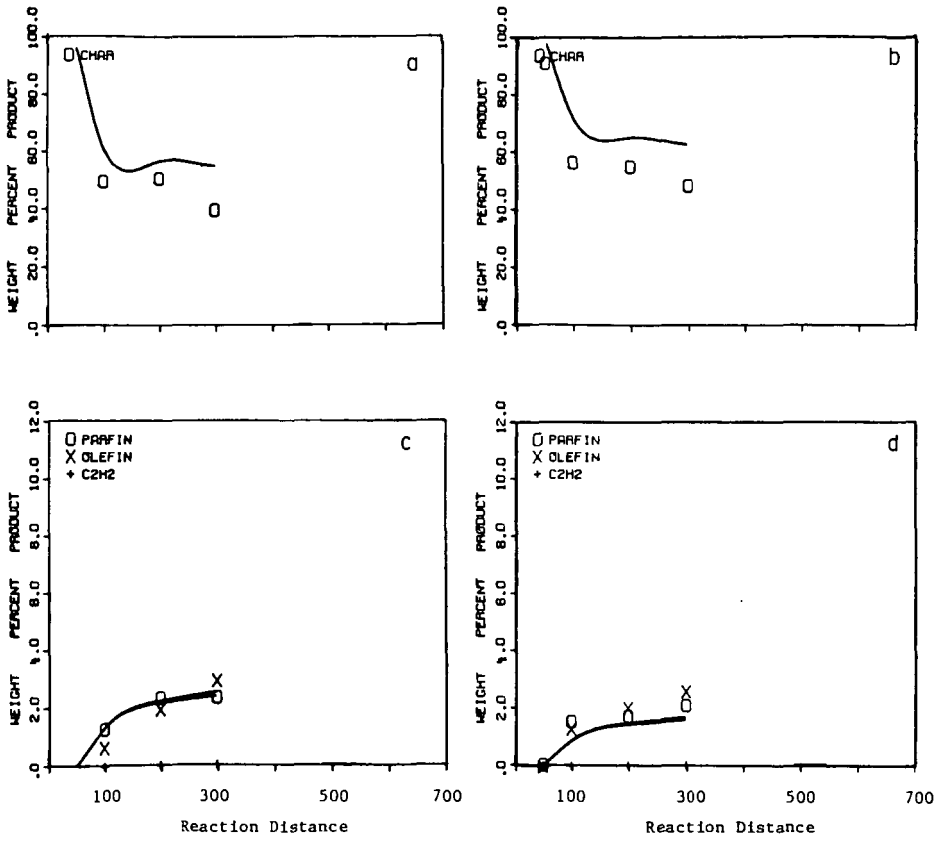

Figure 6. Weight Loss and Evolution of Aliphatic Gases for two Coals Pyrolyzed in the Heated Tube Reactor at an Equilbrium Temperature of 800°C. a and c Illinois #6 and b and d Beulah, North Dakota Lignite.